Comment on "Structure of ferrofluid dynamics"

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We compare known equations for ferrofluid magnetization with a recently proposed *rectified Debye theory* [H. W. Müller and M. Liu, Phys. Rev. E **64**, 061405 (2001)] and demonstrate that the latter is unsatisfactory. Derived by a purely formal method, it contains numerous unknown parameters, fails to explain previous experiments, and has no heuristic force.

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Müller and Liu [1] have proposed a new system of ferrohydrodynamic equations. They claim: "It is important to be aware that we have at our hand a healthy macroscopic theory capable of accounting for all phenomena of ferrofluids." As for the recognized theory [2–4], they declare it to be *a special case* or at least *complementary* to their own ferrofluid dynamics. Below we show that their theory is unsatisfactory.

The conventional theory consists of the phenomenologically derived equation of fluid motion, the Maxwell equations, and the magnetization equation. Just the last undergoes revision from time to time. The point is that for magnetization **M**—unlike energy, momentum, or angular momentum—there is no corresponding conservation law. Therefore, from the angle of formal (phenomenological) thermodynamics, magnetization equation is ill defined: there simply is no place to take it from. For this reason, a peaceful coexistence of *several* phenomenological equations for magnetization of solid magnetic materials became possible. The well-known Landau-Lifshits and Gilbert equations for ferromagnetic, and the Bloch, modified Bloch and Bloch-Bloembergen equations for paramagnetics differ from each other by *relaxation terms*. For ferrofluids there are also possible different magnetization equations. They should only not conflict with thermodynamics, satisfactorily explain known experiments, and predict new phenomena. Hence it is clear: to derive a magnetization equation capable of describing quantitatively experiments on positive [5–8] and negative [9,10] viscosity, on ferrofluid flow induced by rotating magnetic field [11–13], magnetovortical birefringence [14] and vorticomagnetic resonance [15,16], it is necessary to apply some steering *physical idea*. As demonstrated in Ref. [1], the mere observance of Onsager's principle of symmetry of kinetic coefficients is not enough.

Müller and Liu [1] derived their magnetization equation "by means of standard nonequilibrium thermodynamics," that is "from general principles, without reference to the angular momentum of ferromagnetic grains" or to any other specific mechanism. Such a formal application of the common phenomenological method resulted in the equation

$$d\mathbf{M}/dt=\mathbf{\Omega}\times\mathbf{M}+\mathbf{X}^D,$$

$$X_i^D=-(\zeta\delta_{ij}+\zeta_\parallel M_iM_j+\zeta_\times\epsilon_{ijk}M_k)h_j+\lambda_1M_iV_{kk}+\lambda_2M_jV_{ij}^0+\lambda_3M_iM_jM_kV_{jk}^0+\lambda_4\epsilon_{ijk}M_jM_lV_{kl}^0. \quad (1)$$

Here $\mathbf{\Omega}=\frac{1}{2}\nabla\times\mathbf{v}$, $\mathbf{h}=\partial u/\partial\mathbf{M}$ (u is the energy density), $V_{ij}=\frac{1}{2}(\nabla_iv_j+\nabla_jv_i)$, $V_{ij}^0=V_{ij}-\frac{1}{3}V_{kk}\delta_{ij}$, and ζ, $\zeta_\parallel$, $\zeta_\times$, λ_1, λ_2, λ_3, λ_4 represent *seven* unknown coefficients. The authors say that these parameters should be measured, ferrofluid for ferrofluid, but treat them in fact as *fitting parameters*.

Contrary to Eq. (1), the conventional magnetization equations are founded on clear physical concepts and do not contain unknown parameters. The first of them,

$$\frac{d\mathbf{M}}{dt}=\mathbf{\Omega}\times\mathbf{M}-\frac{1}{\tau}(\mathbf{M}-\mathbf{M}_0)-\frac{1}{6\eta\phi}\mathbf{M}\times(\mathbf{M}\times\mathbf{H}), \quad (2)$$

has been derived [2] as a generalization of the Debye relaxation equation, $d\mathbf{M}/dt=-(\mathbf{M}-\mathbf{M}_0)/\tau$, in the case of *spinning* magnetic grains: their angular velocity differs under the field $\mathbf{H}$ from $\mathbf{\Omega}$. In Eq. (2) $\tau=3\eta V/k_BT$ is the Brownian diffusion time, $6\eta\phi$ is the Stokes drag coefficient ($\phi=nV$ is the volume fraction of magnetic grains, n their number density, $V=\pi d^3/6$ is the particle volume), and $\mathbf{M}_0$ stands for the equilibrium magnetization. In a stationary magnetic field $\mathbf{M}_0=nmL(\xi)\ \mathbf{H}/H$, where $\xi=mH/k_BT$, $L(\xi)=\coth\xi-1/\xi$, and $m=M_bV$ is the magnetic moment of a single subdomain particle of a ferromagnetic with the bulk magnetization M_b.

Out of equilibrium, $\mathbf{M}$ ceases to be a function of $\mathbf{H}$. At any moment, however, it can be considered as an equilibrium one in a specially prepared *effective field* $\mathbf{H}_e$ which is tied with $\mathbf{M}$ by the *equilibrium* relation: $\mathbf{M}=nmL(\xi_e)\ \mathbf{H}_e/H_e$, where $\xi_e=mH_e/k_BT$. This introduces $\mathbf{H}_e$ as a new independent thermodynamic variable instead of $\mathbf{M}$. The equation for $\mathbf{H}_e$ [17],

$$\frac{d\mathbf{H}_e}{dt}=\mathbf{\Omega}\times\mathbf{H}_e-\frac{1}{\tau}(\mathbf{H}_e-\mathbf{H})-\frac{1}{6\eta\phi}\mathbf{H}_e\times(\mathbf{M}\times\mathbf{H}), \quad (3)$$

is the second possible phenomenological equation. As shown in Ref. [17], Eqs. (2) and (3) agree well with general principles, i.e., both of them are correct from the standpoint of thermodynamics. They are valid in a stationary or low-frequency magnetic field [18] and coincide with each other in the weak field limit, $\xi\ll1$, when the true magnetization and its equilibrium value take the form $\mathbf{M}=\chi\mathbf{H}_e$ and $\mathbf{M}_0=\chi\mathbf{H}$, where $\chi=nm^2/3k_BT$ is the initial magnetic susceptibility.

Finally, in an oscillating magnetic field of a high amplitude ($\xi>1$) and frequency ($\omega\tau>1$), one should employ the

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effective field theory (EFT). The latter represents the magnetization equation derived *microscopically* [19] from the Fokker-Planck equation. Predictions of EFT are well corroborated by all known experiments and direct numerical methods [20,21]. The EFT performs better than phenomenological Eqs. (2) and (3): the potential of microscopic theory is much greater than that of any macroscopic approach. Thus we feel the declaration [1] ''Theoretically, there never was any reason to give Debye less credit than EFT'' is wrong in principle.

The authors claimed: ''Both the Debye theory [Eq. (2)] and the effective field theory by Shliomis are shown to be *special cases* of the new set of equations [Eq. (1)].'' To confirm this statement, they offered ''the following *particular choice*'' of their free parameters: $\lambda_1=\lambda_2=\lambda_3=\lambda_4=\zeta_\times=0$,

$$\zeta=\frac{M_0}{\tau H}+\frac{M_0^2}{6\eta\phi},\quad \zeta_\parallel=\frac{1}{\tau M_0^2}\left(\frac{\partial M_0}{\partial H}-\frac{M_0}{H}\right)-\frac{1}{6\eta\phi}.$$

Such expressions evidently cannot be guessed. Hence this *choice* displays the need of the conventional theory to fill the formal scheme [1] with a physical meaning.

Müller and Liu (ML) especially emphasize in Eq. (1) the term with λ_2 coefficient, since it ''shows that in addition to the vorticity $\mathbf{\Omega}$, compressional and elongated flow may also contribute to the dynamics of $\mathbf{M}$.'' They do not point out, however, any physical reason for the contribution. Meanwhile such a term was introduced long ago [22] to generalize the theory [19] in the case of *nonspherical* magnetic grains. Indeed, even in a symmetric flow ($\Omega_i=0, V_{ik}\neq 0$) they revolve with an angular velocity $A_{ikl}V_{kl}$, where A_{ikl} depends on the particle shape. All components of the tensor vanish for a sphere: symmetric flow cannot rotate a spherical grain and thereby cannot alter an orientation of its magnetic moment. Martsenyuk [22] has considered magnetic grains of arbitrary shape and shown that there are seven independent components of ferrofluid viscosity in the general case and six components for suspension of uniaxial ellipsoids (with semiaxes $a\neq b=c$). He has found the viscosity coefficients as *explicit* functions of the field ξ and the parameter of nonsphericity $\kappa=(a^2-b^2)/(a^2+b^2)$, whereas ζ_i and λ_i in Eq. (1) are *unknown* functions of these parameters. (For quasispherical particles, $\kappa\ll 1$, the theory [22] gives $\lambda_2\propto\kappa$). So, as usual, statistical thermodynamics *yields more* than the phenomenological one.

Müller and Liu [1] wrote: ''When the negative viscosity experiment of Bacri *et al.* [9] contradicted the *Debye theory*, Shliomis referred to a more elaborate evolution equation for $\mathbf{M}$ [19]'' (the references are numbered here as in the Comment). The above statement misrepresents the facts. First, the negative viscosity has been predicted [23] just on the basis of Debye-like Eq. (2). Second, this prediction contradicts neither experiment [9] nor EFT. Maps of rotational viscosity η_r in a harmonically varying magnetic field are displayed in Figs. 1 and 2. The isoline $\eta_r(\xi_0,\omega\tau)=0$ divides the amplitude-frequency plane into two parts: the left-hand part of the positive viscosity and the right-hand part of the negative one. As seen, the figures are rather alike. Experimentally obtained isolines [9,10] are very similar to those in Fig. 2.

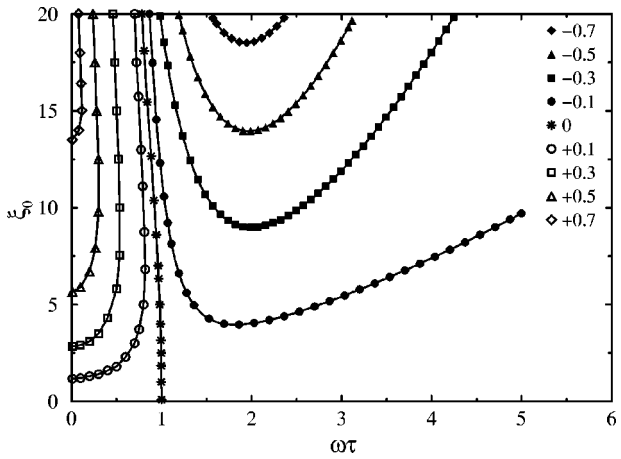

FIG. 1. Map of viscosity, the isolines of reduced viscosity $\eta_r(\xi_0,\omega\tau)/\eta_r(\infty,0)=C$ for $-0.7\leqslant C\leqslant+0.7$ in the plane of dimensionless field amplitude ξ_0 and frequency $\omega\tau$, as calculated from Debye-like Eq. (2). Here $\eta_r(\infty,0)=3\eta\phi/2$ (the saturation value).

ML presented their own explanation of the experiment [9]. Assuming $\lambda_1=\lambda_2=\lambda_3=\zeta_\parallel=\zeta_\times=0$ and $\mathbf{h}=\mathbf{H}_e-\mathbf{H}$, they reduced Eq. (1) to the equation

$$d\mathbf{M}/dt=\mathbf{\Omega}\times\mathbf{M}-\zeta(\mathbf{H}_e-\mathbf{H}),\tag{4}$$

which they have referred to as the *rectified Debye* theory. In fact, however, this equation represents a curtailed *hybrid* of Eqs. (2) and (3): the relaxation term $\zeta(\mathbf{H}_e-\mathbf{H})$ belonging to Eq. (3) is substituted into Eq. (2) instead of its own term $(\mathbf{M}-\mathbf{M}_0)/\tau$.

Generally, the Debye equation is fundamental as much as the very irreversible thermodynamics and has no need for any rectification. In accordance with principal propositions of the theory, the rate dz/dt of change of any value z is determined by the *same value* at the same moment: $dz/dt=f(z,t)$. So, if z weakly deviates from its equilibrium value z_0, one can expand $f(z)$ over $z-z_0$. Confining oneself to the

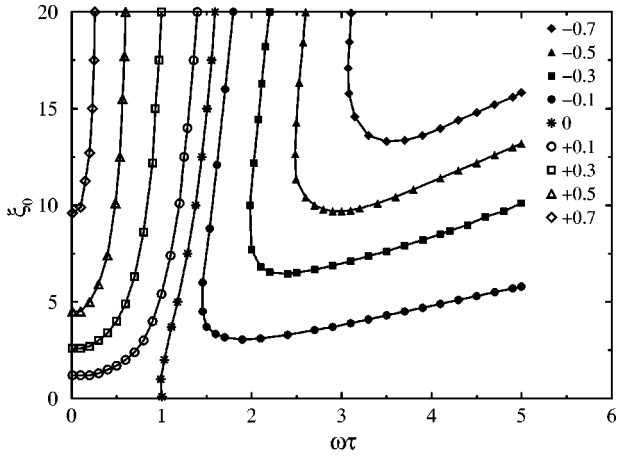

FIG. 2. Same as in Fig. 1, but calculated by EFT.

linear term, we arrive at the Debye relaxation equation $dz/dt=-(z-z_0)/\tau$. Let us suppose now that z is a function of x and reaches its equilibrium $z=z_0$ at $x=x_0$. Then the function $dz/dt=f(z(x))$ can be expanded over $x-x_0$, which results in the *rectified Debye* equation $dz/dt=-\zeta(x-x_0)$ using ML terminology. However, the coefficient ζ—unlike τ in the true Debye equation—is not a constant but represents a function of x_0. Only in the low field limit, when $\mathbf{M}=\chi\mathbf{H}$, does ζ reduce to the constant, $\zeta=\chi/\tau$, whereupon Eq. (4) transforms into *linearized* Eq. (2). But for a finite magnetic field strength, ζ is an *unknown function* of H.

Authors of the theory [1] claimed: ''Employing Eq. (4), we reevaluated the experiment [9] and found convincing agreement, see Fig. 1.'' Although the figure clearly demonstrates the absence of any agreement, it is worth looking at the way the agreement is achieved.

First, in Sec. II A it is asserted that the *rectified Debye* Eq. (4) is valid only in the weak field limit, $\xi\ll 1$. Later on, however, this equation is used up to $H=3000$ Oe (see Fig. 1 in Ref. [1]), i.e., to $\xi\simeq 15$. In such a strong field the *nonlinear* relaxation term (with the double vector product) belonging to Eqs. (2) and (3) but *missing* in Eq. (4) predominates over the linear term and then should be taken into account *without fail*.

Further, to fit the data measured in Ref. [9] one needs to know some fluid parameters. ''For lack of pertinent ferrofluid specification,'' the authors ''used the saturation magnetization $M_s=127$ G and the initial susceptibility $\chi=1$.'' The authors' desire to have two additional fitting parameters looks strange at least, because all necessary data for M_s and χ are given in Ref. [9]. Indeed, we find there the bulk magnetization of the cobalt ferrite particles $M_b=400$ G, the volume fraction of the particles $\phi=20\%$, and their mean diameter $d=10$ nm. Multiplying M_b by ϕ we immediately obtain $M_s=80$ G, which is far from the value 127 G used in Ref. [1]. Substituting then M_b, M_s, and d in the relationship $\chi=\pi d^3 M_b M_s/18k_BT$, we get $\chi=0.14$ [24] which is also far from unity.

Finally, two enigmatic curves featured in Fig. 1 of Ref. [1] allegedly represent the EFT results ''as gleaned from Fig. 4 of Bacri *et al.* [9].'' But in the last figure there are no such data at all.

One more experiment of the Bacri group [16] is considered in Ref. [1]. This fundamental experiment has displayed a close connection between the *negative viscosity* and the *vorticomagnetic resonance*. Ferrofluid was exposed to solid rotation with an angular velocity $\mathbf{\Omega}$ around the axis of cylinder (axis z) in an oscillating magnetic field $H_x=H_0\cos\omega t$. The rotational viscosity η_r and the off-axis component of magnetization $M_y=\chi_\perp H_x$ were measured simultaneously. According to Eq. (2), η_r changes its sign and $|\chi_\perp|$ has the maximum at the same field frequency, $\omega\approx\Omega$, if $\Omega\tau$ is large enough. Predicted dependencies have appeared, however, *too smooth* in comparison with the experimentally observed *sharp-edge* resonance peak of M_y and the *steep fall* of η_r near $\omega=\Omega$. Such a behavior gives sure signals of the presence of a *wide spectrum* of relaxation times τ instead of only one Brownian time τ_0 for single magnetic grain. It has been supposed [16] that the spectrum originates from *chains* formed out of the grains. The probability P_N of N-particle chain formation depends on the parameter of magnetodipole interaction $\epsilon=2m^2/d^3k_BT$ and the particle concentration ϕ. Averaging the single-particle expressions for η_r and $|\chi_\perp|$ over the chain lengths with the distribution function P_N has yielded a *perfect agreement* with experimental data of Ref. [16]. The best fit was reached with the value $\epsilon=5$, which is close to an independent evaluation $\epsilon=5.3$ coming from measurements. The function P_N has made it possible to compute the mean magnetization relaxation time $\langle\tau\rangle=5.2\tau_0$. Contrary to the case of solid rotation, neither the resonance of $|\chi_\perp|$ nor the drastic fall of η_r was obtained for a Couette shear flow. It indicates that long relaxation times associated with the most long chains do not exist any more in the spectrum: the shear *fractures* the chains.

To describe the experiment [16] by Eq. (1), ML kept in $\mathbf{X}^D$ two terms—with coefficients ζ and λ_2. For the flow under consideration, $v=v_\varphi(r)$, both the vorticity $\Omega_{ik}=\epsilon_{ikl}\Omega_l$ and the shear rate V_{ik} have single nontrivial component: $\Omega_{r\varphi}=(dv/dr-v/r)/2, V_{r\varphi}=(dv/dr+v/r)/2$. In the case of solid rotation, $v=\Omega r$, there are $\Omega_{r\varphi}=\Omega$ and $V_{r\varphi}=0$, so the λ_2 term vanishes whereupon Eq. (1) leads to the relationships of Ref. [16] with $\tau=\chi/\zeta$. The authors treat τ as a fitting parameter but do not indicate its value used for the fitting. Analyzing their Fig. 2(a), we conclude they took $\tau=27$ ms, which is 17 times larger than the single-particle time $\tau_0=1.6$ ms and 3.2 times larger than the mean relaxation time $\langle\tau\rangle$. However, neither this incongruous value of τ nor any other *sole* relaxation time can provide a satisfactory agreement with the experiment [16]. As noted above, such an agreement is reached only with due regard for the wide spectrum of magnetization relaxation times. Miller and Liu [1] estimated λ_2 from fitting the decay of $|\chi_\perp|$ in the shear flow case ($\Omega_{r\varphi}\neq V_{r\varphi}\neq 0$). Their estimate $\lambda_2=2.54$ does not instill a confidence since for the fitting they used the same odd value of $\tau=27$ ms.

In conclusion, the pure formal approach to the construction of ferrofluid dynamics [1] would have been perhaps appropriate 30 years ago, i.e., *before* the modern ferrohydrodynamics was created. Of course, the existing theory is incomplete and open to criticism. First of all, it should be generalized in the case of large coupling constant, $\epsilon\simeq 10$, and high particle concentration, $\phi\simeq 20\%$. Both these factors lead to association of magnetic grains into the abovementioned chains and clusters. Such a generalization demands methods that are not formal and calls for new physical ideas. An important place among them will be taken by concepts of polymer physics. Some of them have already been applied well in the physics of magnetic colloids. As for Ref. [1], we see no reason to believe that this theory, which is not able to describe satisfactorily even *dilute* magnetic colloids, would now be valid for *dense* ones.

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